

Oxygen isotope composition of mantle minerals by laser fluorination analysis: homogeneity in peridotites, heterogeneity in eclogites

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Introduction

The oxygen isotopic composition of 102 nodules of spinel-, garnet- and diamond-facies peridotites and 62 nodules of diamondiferous-, non-diamondiferous and kyanite-eclogites have been determined by laser fluorination (LF). The small sample sizes required, 100% oxygen yields and the high precision of the LF data allows the study of inter-grain isotopic variations, the detailed analysis of fractionation between co-existing phases, and discussion of isotopic equilibrium at mantle temperatures. The dataset represents a comprehensive and diverse range of lithological and geochemical types and is of similar size to the complete published dataset for these rock types derived by classical fluorination (CF) techniques.

Methods

The LF technique used in this study is described by Matthey & Macpherson (1993). Mineral grains free of inclusions and secondary alteration were selected for analysis. Approximately 1.0–1.5mg of sample (commonly 5–10 grains) were heated using a Nd:YAG laser in the presence of ClF_3 . Oxygen is converted to CO_2 over hot graphite. Replicate analyses of the same phase normally fall within 0.1‰ of each other. The LF oxygen isotope data are calibrated to V-SMOW and NBS-30 biotite (5.10‰). A San Carlos olivine (SC ol) is used as a secondary 'house' standard with each batch of samples. This has a mean $\delta^{18}\text{O}$ value of $4.86 \pm 0.18\text{‰}$ (2sd, $n = 245$) and an average yield of $100.9 \pm 2.1\%$.

Results

Peridotites. $\delta^{18}\text{O}$ values of olivines are almost invariant, averaging $5.19 \pm 0.26\text{‰}$ (2sd, $n = 94$), with an overall range from 4.8‰ to 5.5‰. Co-existing clinopyroxenes average $5.61 \pm 0.32\text{‰}$ (82) and orthopyroxenes $5.73 \pm 0.32\text{‰}$ (76).

Mean $\Delta^{18}\text{O}_{\text{cpx-ol}}$ and $\Delta^{18}\text{O}_{\text{opx-ol}}$ values are clearly distinct at $0.39 \pm 0.04\text{‰}$ and $0.54 \pm 0.04\text{‰}$ (2se, $n = 74$ and 71, respectively). The $\Delta^{18}\text{O}_{\text{cpx-ol}}$ fractionations are consistent with isotopic equilibrium at temperatures averaging 1200°C (Chiba *et al.*, 1989). Both orthopyroxene and clinopyroxene have ranges of 0.7‰, the same as for olivine. Spinel averages $4.37 \pm 0.66\text{‰}$ (2sd, $n=20$) in spinel facies peridotites and garnet averages $5.37 \pm 0.36\text{‰}$ (44) in garnet facies peridotites. The dominant hydrous phase in spinel-peridotites is amphibole with a mean of $5.36 \pm 0.30\text{‰}$ (13), the dominant hydrous phase in garnet-peridotites is phlogopite with a mean of $5.74 \pm 0.53\text{‰}$ (16). Variations in the mean $\delta^{18}\text{O}$ of the main mineral phases is insignificant between hydrous and anhydrous lithologies. Even where the hydration and recrystallisation is extreme, as in MARID samples from Bultfontein, the deviations from the norm are small with clinopyroxene at 5.94‰ and phlogopite at 6.06‰.

Eclogites. The $\delta^{18}\text{O}$ values range from 2.4‰ to 7.4‰ for garnet and from 2.8‰ to 7.4‰ for clinopyroxene. All samples show positive $\Delta^{18}\text{O}_{\text{cpx-gt}}$ values ranging from 0.0‰ to 0.6‰ and averaging 0.31‰. A suite of kyanite eclogites from Roberts Victor Mine, RSA, are all enriched in ^{18}O (+5.9‰ to +7.4‰) compared to LF mantle peridotite values, and have positive $\Delta^{18}\text{O}_{\text{ky-gt}}$ values ranging from 0.1‰ to 0.6‰, similar to the range of $\Delta^{18}\text{O}_{\text{cpx-gt}}$ values recorded for normal eclogites.

Comparison of LF and CF data for mantle lithologies

LF $\delta^{18}\text{O}$ data for peridotites are in marked contrast to $\delta^{18}\text{O}$ values obtained by CF techniques (Fig. 1; see Matthey *et al.*, submitted, and references cited therein). The latter have significantly greater ranges, most notably for olivine (4.4‰ to 7.5‰ - CF, 4.8‰ to 5.5‰ - LF) and highly variable $\Delta^{18}\text{O}_{\text{cpx-olv}}$ fractionations (–1.42‰

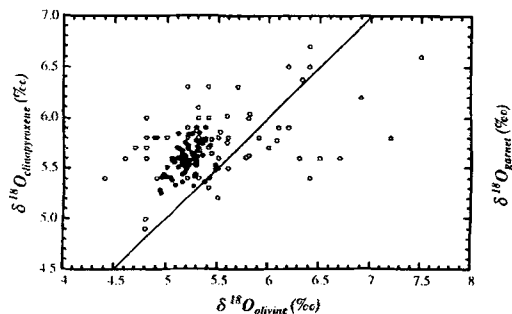


FIG. 1. Comparison of LF and CF $\delta^{18}\text{O}$ data for spinel- and garnet-peridotites shown on a plot of $\delta^{18}\text{O}_{\text{Ool}}$ versus $\delta^{18}\text{O}_{\text{Cpx}}$. Filled circles = data obtained in this study by LF. Open circles = data obtained by CF reported in the literature (see text for references). A line corresponding to $\Delta^{18}\text{O}_{\text{Cpx-ol}} = 0$ is shown for reference.

to 1.2‰ - CF, 0.0‰ to 0.9‰ - LF). The high percentage (~90%) of LF samples which show oxygen isotopic equilibrium between the main mineral phases, is not typical of published CF data (<40%). Re-analysis of some of these CF samples (Kyser *et al.*, 1981; 1982; Kyser, 1990) further highlights the discrepancies between LF and CF analyses. The discrepancy is largest for olivines (up to 1‰), but generally <0.3‰ for pyroxenes (Mattey *et al.*, submitted). The LF and CF techniques provide equivalent data (within error) for less refractory phases such as biotite, ilmenite and quartz (Mattey *et al.*, submitted).

The range of LF $\delta^{18}\text{O}$ data for garnet and clinopyroxene in eclogites (2.4‰ to 7.4‰) closely resembles the reported range for published CF data (2‰ to 8‰) (Fig. 2; e.g. MacGregor & Manton, 1986; Neal *et al.* 1990, Deines *et al.*, 1991). However, there are a significant number of reversed $\Delta^{18}\text{O}_{\text{Cpx-gt}}$ fractionations in published CF data, which are totally absent from the LF dataset (-0.9‰ to +1.0‰ - CF, 0.0‰ to 0.6‰ - LF) (Fig. 2).

Discussion and conclusions

The new data obtained by laser-fluorination are believed to portray a more accurate picture of oxygen isotope systematics in the mantle, which are far less complicated than previously thought. Prior to this study the debate focussed on whether oxygen isotope heterogeneity was a widespread characteristic of the mantle (Kyser *et al.*, 1981; 1982) or a more local phenomenon related to metasomatic enrichment (e.g. Gregory & Taylor, 1986). The isotopic disequilibrium between olivine and clinopyroxene displayed by many conven-

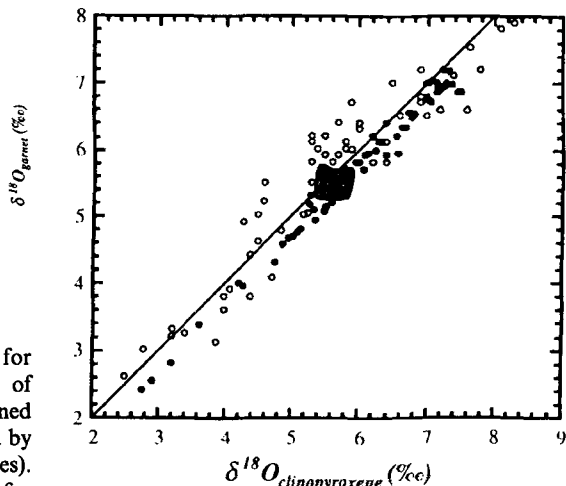


FIG. 2. Comparison of LF and CF $\delta^{18}\text{O}$ data for eclogites shown on a plot of $\delta^{18}\text{O}_{\text{Cpx}}$ versus $\delta^{18}\text{O}_{\text{gt}}$. Filled circles = data obtained in this study by LF. Open circles = data obtained by CF reported in the literature (see text for references). The shaded area represents the restricted field of LF data for mantle peridotites. A line corresponding to $\Delta^{18}\text{O}_{\text{Cpx-gt}} = 0$ is shown for reference.

tional analyses have previously been interpreted as a result of open-system interactions with fluids possessing exotic oxygen isotope compositions derived from subducted oceanic crust. Such processes are not required to explain the variations in the LF oxygen isotope data of peridotites. There is also little evidence that mantle hydration processes impart distinctive oxygen isotope characteristics in peridotites other than rare shifts of <0.4‰ disturbing pyroxenes relative to olivine which may represent a localised phenomenon. When the LF data are taken to represent the best estimate of peridotitic mantle, nearly 75% of LF eclogite $\delta^{18}\text{O}$ data fall outside the peridotite range. This further strengthens arguments which invoke subducted slab as the source for many mantle eclogites.

References

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